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The aim of this project initially was to develop accurate non-parametric methods for determining the energy band structure of semi-conducting polymers and then to incorporate within the same model a method to determine the electron levels due to impurity atoms used as replacements for the side groups about the polymer back bone. Secondly, we were to study the energy structure of several polymers with and without impurity side groups. These tasks have been successfully accomplished.

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ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES OF

SEMI-CONDUCTING POLYMERS

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The aim of this project initially was to develop accurate non-parametric methods for determining the energy band structure of semi-conducting polymers and then to incorporate within the same model a method to determine the electron levels due to impurity atoms used as replacements for the side groups about the polymer back bone. Secondly, we were to study the energy structure of several polymers with and without impurity side groups. These tasks have been successfully accomplished.

The essential approximation employed here is that of Hartree-Fock. Here the many body Hamiltonian is simply:

$$H = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i,I} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i,j}' \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{I,J}' \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} . \quad (1)$$

The trial wavefunction has the form:

$$\psi(\vec{r}_1 \ldots \vec{r}_N) = \frac{1}{\sqrt{N!}} \det|\phi_i(\vec{r}_i)| . \quad (2)$$

Here we use atomic units, $e = \hbar = m = 1$, length in a.u. (1 a.u. $\simeq .53 \text{Å}$) and energy in Hartree's (1 Hy = 27.2 eV). Lower case letters refer to electron properties and upper case to nuclear properties. If we constrain the ϕ's to be orthonormal and eigenstates of s_z and require that the expectation value of H be minimized with respect to our trial ψ, then the ϕ's are determined by the unrestricted Hartree-Fock eq.:

$$F\phi_i = \varepsilon_i \phi_i . \quad (3)$$

Here

$$F = -\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\vec{r} - \vec{R}_I|} + \sum_{j=1}^{N} \int \frac{\phi_j^2(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

$$-\sum_{j=1}^{N} \phi_j(\vec{r}) \phi_j^+(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \hat{P}(\vec{r}\vec{r}') . \quad (4)$$

$\hat{P}(\vec{r}\vec{r}')$ is the operator which interchanges coordinates $\vec{r}$ and $\vec{r}'$. It is this set of equations which we will solve. The final results will have one well characterized deficiency. The usual Hartree-Fock solution has too great a gap between the uppermost occupied orbital (HOMO) and the least unoccupied virtual orbital (LUMO). This deficiency has been well studied in both polymer and solid state systems[1] and is only of concern when one needs the value of the gap precisely. In any event this deficiency may be readily corrected by using the electronic polaron for long range correlation[2] and $\Delta E(SCF)$ techniques for short range orbital relaxation[3]. The internal band details are far less sensitive to such corrections. For the express purposes of this report we ignore such corrections other than to say their inclusion is quite trivial.

The essential problems in solving the system of equation (4) lie in that some simplifying assumptions are needed still, and it is with these that we initially concern ourselves. To see the problems and procedure, consider as a prototype system polyethylene, which has a unit:

```
     H   H
     |   |
 — : C — C —
     |   |
     H   H        .
```
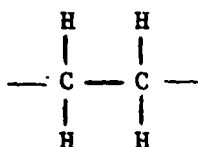
This unit is repeated infinitely. If one uses energy band techniques, this repetition must have one dimensional translational symmetry and hence one must idealize out of existence the random twisting of the backbone of such a polymer which occurs in the real world. Additionally, in the infinite system Ewald sums occuring in F yield a poorly defined energy zero and thus accurate positioning of impurity levels without use of methods such as Stater-Koster becomes hard.

There is an alternate approach. This is to reduce the polymer to a finite size. This is the cluster problem.[4] Here the essential approximation is to reduce an infinite size system to a small, finite one. In doing this one loses the $\epsilon(\vec{k})$ curves, beloved of the band theorist, but retains a set of energy levels which have no $\vec{k}$ label. These levels form a state density which is consistent with those of energy band theory provided one: a) uses proper boundary conditions on the cluster[5]; b) uses a large enough cluster.[6] The use of clusters compensates for these problems by permitting one to study non-ideal geometries, and by allowing simple inclusion of defects or impurities in the calculation. We tried both methods initially and decided finally that the cluster techniques were to be preferred for this study. In the remainder of this report we concentrate on cluster results.

The size of cluster has been investigated by J.-M. Andre and J. Delhalle for the case of polyethylene using the Extended Huckel method.[6] They study the energy levels for clusters of 1, 2, 3, 4, 5 and 6 C-atoms and for the idealized band geometry (∞ C-atoms). Essentially, the results are fully converged in band position with 1 C-atom and in width with 4 C-atoms. In our study we use 6 C-atoms in the backbone as a guarantee of convergence. The second problem is the finite cluster termination. Polyethylene is a covalent system and according to the prescription of Kunz and Klein one should place an excess electron and nucleus at each end of the intercepted chain.[5] Conventionally one chooses a proton for the replacement nucleon[4], but it has been observed by Allen that one may vary the charge of this nucleon to force the atoms at the end of the chain to have core properties similar to those in the center.[7] We concur with this suggestion and used it here. We found, however, when the charge was varied in units of 0.1 electron charges for our system that

a value of 1 (the proton charge) was in fact optimal. We believe this is consistent with polyethylene being an essentially pure covalent system.

The cluster energy levels for polyethylene are shown in Figure 1 for the valence levels as given in our calculation. In addition the density of States for polyethylene in all available alternate models using band theory are shown in Figure 1 as well by means of comparison. It is clear that a reasonable agreement exists between our UHF results and the existing ab initio result.[8] Agreement with the other results all of which are either highly approximate or parametric is less good. These include F.S.G.O.[9], L.C.L.O.[10], E.H.C.O.[11], CNDO/2[11] and CNDO/2[11] methods. The disagreement, small though it is, between our UHF results and the ab initio results probably reflects the level of Hartree-Fock achieved in the ab initio results and the integral approximations used rather than the finite cluster size. We use a gaussian basis set of double zeta accuracy here and evaluate all our integrals exactly to the precision permitted by our computer (8.5 significant figures here). We conclude that our technique produces a viable energy level scheme for the polymer of interest and is competitive in this respect to energy band calculations. A like study was performed for a Si based polymer in a hypothetical structure similar to polyethylene. Results were quite similar.

The final study concerned the doping of the polymer chain with impurity. In this event a hydrogen was removed from an internal C(Si) and an impurity substituted. In the case of $[CH_2]_N$ we used Li, Be, B and F and for $[SiH]_N$ we used Li, Be and F. We attempted to see if for polyvalent impurities, in this case Be on $[ScH]_N$, one could remove a second H atom as well. We find this to indeed be a lower energy state however, the one electron energy levels are not much modified by this and we ignore this complexity in the other studies.

The one electron H.F. levels for $[CH_2]_N$ and with Li, Be, B, and F are seen in figure 2 and for $[SiH_2]_N$ and with Li, Be and F in figure 3. It is clear from these figures that the effect of the impurity is to allow the occupied levels to remain largely undisturbed, except that occupied levels are now found in the energy gap. The effect on the virtual levels is far more pronounced and causes the formation of local trap states below the conduction band. The apparent number of these is much exaggerated here due to the finite size of the cluster. In actuality, the electronic structure would look like a superposition of the perfect polymer structure and that shown including impurity. Finally, we observe here that including correlation effects would reduce the band gap by about 0.2 Hy. Thus, we further conclude that proper modification of side groups in the semiconducting polymers offers a viable means of gap modification but also introduces the hazard of trapping states in the gap. In this respect such systems behave much as ordinary semiconductors.

The results obtained are being combined into form to submit for publication.

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Figure Captions

Figure 1: The one electron occupied valence levels of polyethylene from our study are shown in <u>a</u>. In <u>b</u> we find a state density for this system from ab initio energy band theory, in <u>c</u> we see like results using a FSGO method, in <u>d</u> using a LCLO method, in <u>e</u> using the EHCO method, in <u>f</u> using the CNDO/2 method and in <u>g</u> using a CNDO/w method.

Figure 2: The one electron energy levels, both occupied and virtual for polyethylene, including impurities are seen for several cases. The fermi energy, ε_f, is indicated.

Figure 3: The one electron energy levels, both occupied and virtual for $[SiH_2]$, including impurities are seen for several cases. The fermi energy, ε_f, is shown.
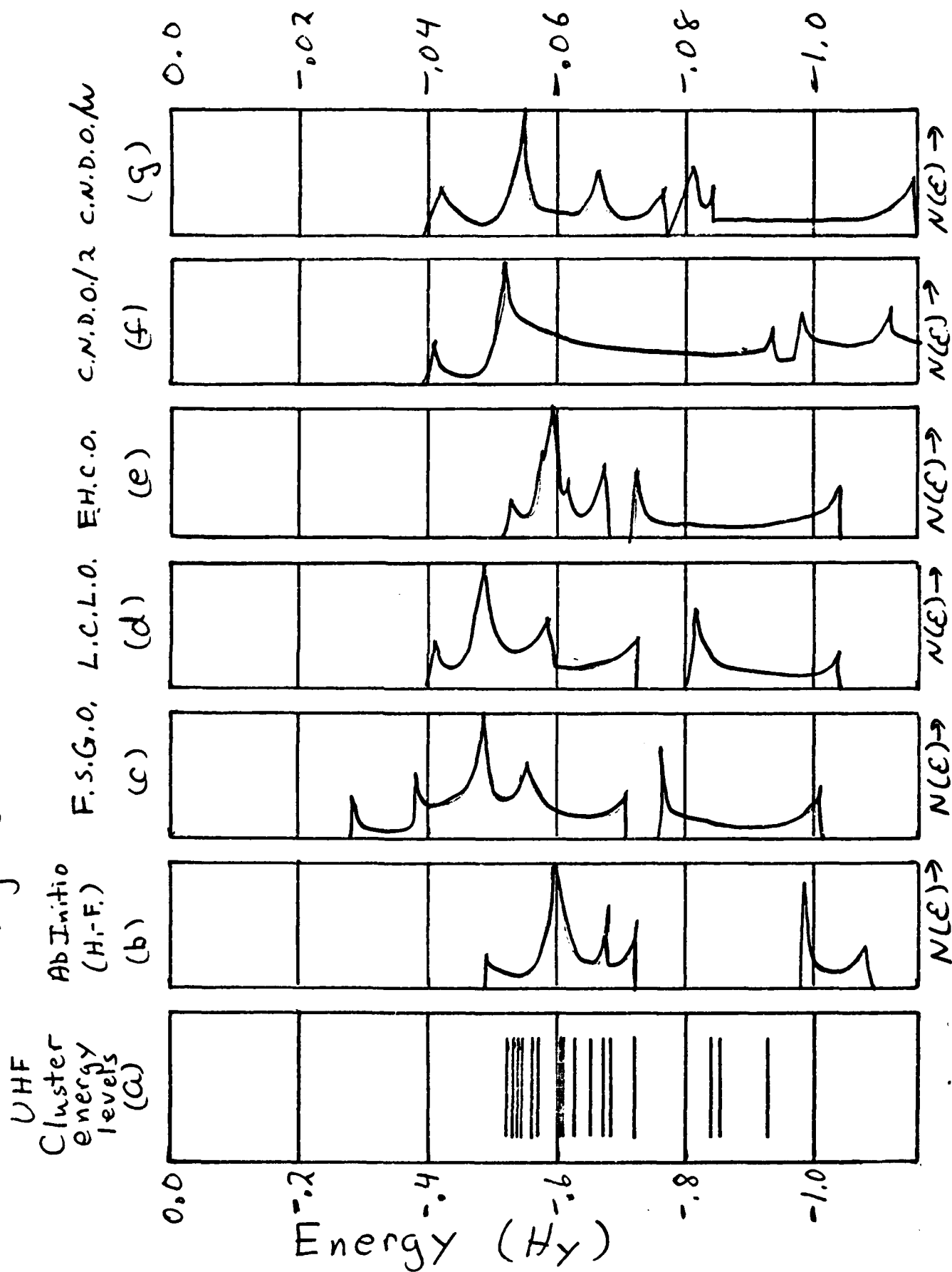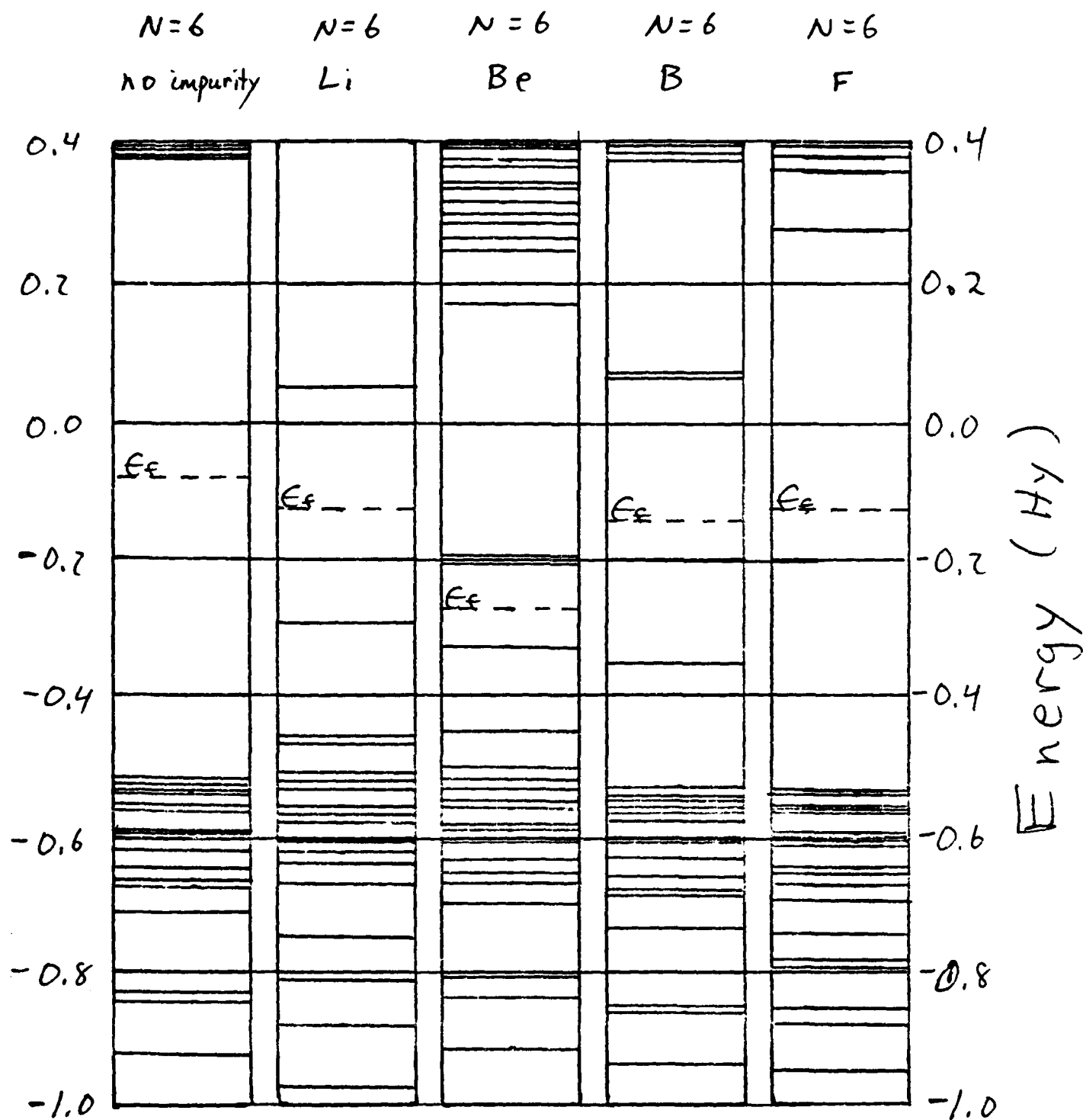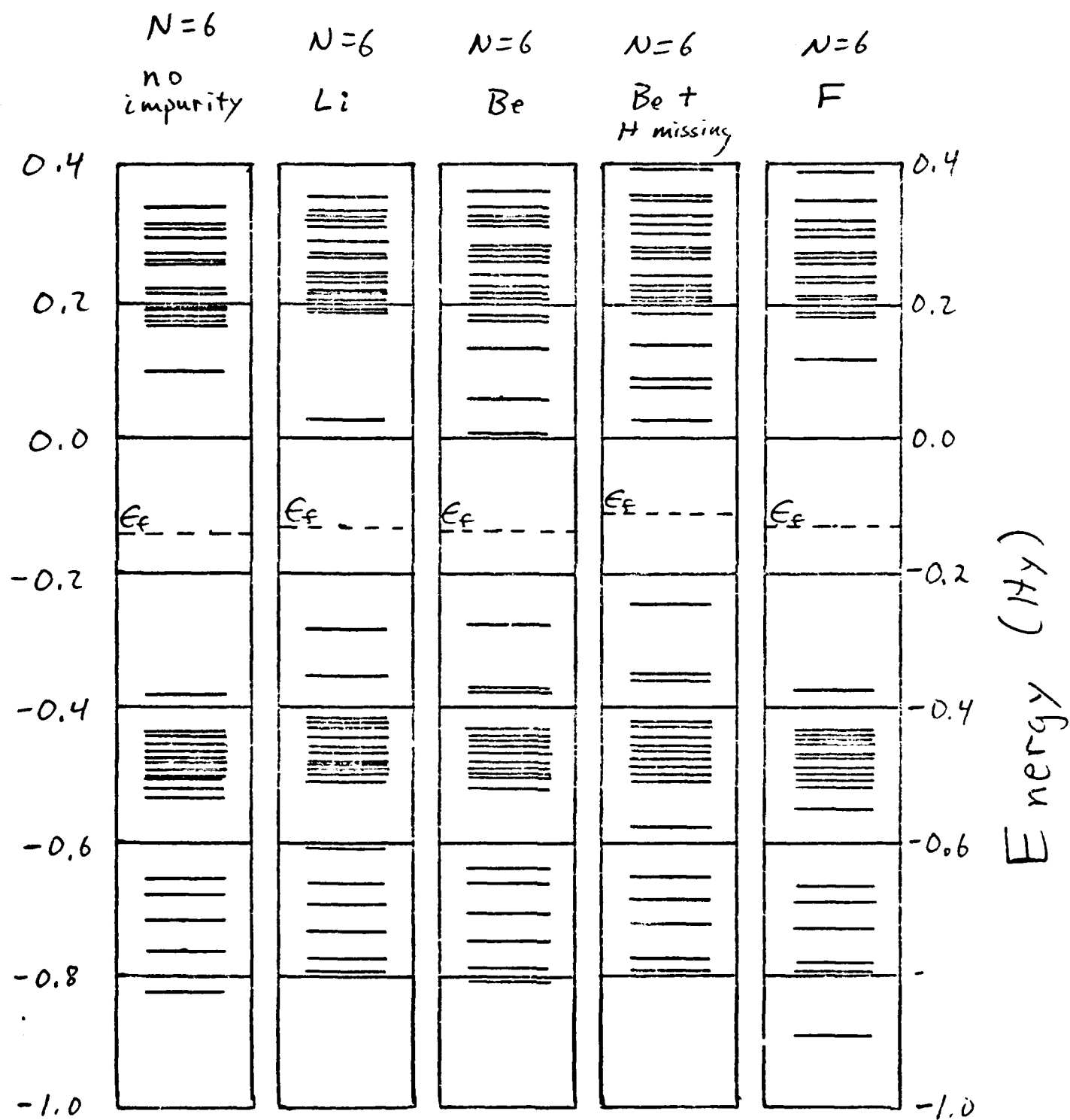
Figure 1

Figure 2
$[CH_2]_N$

N=6 no impurity · N=6 Li · N=6 Be · N=6 B · N=6 F

Energy (Hy)

Figure 3

$[SiH_2]_N$

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